



Short communication

A novel method for effective diffusion coefficient measurement in gas diffusion media of polymer electrolyte fuel cells

Linlin Yang^{a,b}, Hai Sun^a, Xudong Fu^{a,b}, Suli Wang^a, Luhua Jiang^a, Gongquan Sun^{a,*}^a Division of Fuel Cell & Battery, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China^b University of Chinese Academy of Sciences, Beijing 100039, China

HIGHLIGHTS

- A novel method for measuring effective diffusion coefficient is developed.
- Establishment of O₂ concentration difference is realized in an air-breathing PEMFC.
- The O₂ concentration differences are correlated with the PEMFC voltage differences.
- This method is more reliable than conventional conductivity method.

ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form

26 September 2013

Accepted 1 October 2013

Available online 4 December 2013

Keywords:

Effective diffusion coefficient

Porous material

Carbon paper

Fuel cell

ABSTRACT

A novel method for measuring effective diffusion coefficient of porous materials is developed. The oxygen concentration gradient is established by an air-breathing proton exchange membrane fuel cell (PEMFC). The porous sample is set in a sample holder located in the cathode plate of the PEMFC. At a given oxygen flux, the effective diffusion coefficients are related to the difference of oxygen concentration across the samples, which can be correlated with the differences of the output voltage of the PEMFC with and without inserting the sample in the cathode plate. Compared to the conventional electrical conductivity method, this method is more reliable for measuring non-wetting samples.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Transport phenomena in porous media has long been an important research subject because of the wide-ranging application of the porous materials in separation, catalysis, energy transformation and storage, and so on. A thorough understanding of the mass transport limitations in gas diffusion material (GDM) is crucial to provide insight into GDM design, as well as to improve the fuel cell performance. There are several mechanisms for mass transport in porous media: (i) ordinary diffusion, (ii) Knudsen diffusion, (iii) viscous flow, (iv) surface diffusion. It is a meaningful but challenging task to predict the effective diffusion coefficient in porous media, since no completely satisfied theory is available [1].

Gas diffusion coefficients can be measured by whether steady state (constant concentration boundary condition) or transient

state methods (time-dependent concentration boundary condition) [2], such as closed-tube (Loschmidt), two-bulb, evaporation-tube, point-source method and so on; a detailed survey of this field can be found in reference [3]. All the methods involve establishing a concentration gradient and monitoring the flux (or gas concentration), usually requiring specially constructed diffusion cells and tracer/carrier gas [2–6]. Several researchers investigated *in situ* limiting current density of an operating fuel cell to characterize the mass transport properties of gas diffusion media in membrane electrode assembly (MEA) [7–11], however, one specified MEA need to be prepared for each test and the value measured is an overall mass transfer coefficient arising in flow channel, backing layer, microporous layer (MPL) and catalyst layer.

As Fick's first law is analogous to Ohm's law in mathematics, the determination of the effective conductivity can be translated immediately into equivalent results for the effective diffusion coefficient [12,13]. Researchers tend to measure the correction factor of diffusion coefficient, N_M , i.e., the MacMullin number, which is

* Corresponding author. Tel./fax: +86 0411 84379063.

E-mail address: gqsun@dicp.ac.cn (G. Sun).

defined as the ratio of the resistivity of the porous media filled with electrolyte to the bulk resistance of the same electrolyte, based on electrical properties since the conductivity is easy to be measured [14–16]. N_M is a function of porosity (ϵ), tortuosity (τ) and the pore size distribution and connectivity [15,16]. Then the effective diffusion coefficient D_e can be expressed as:

$$D_e = \frac{D_o}{N_M} \quad (1)$$

where D_o is the diffusion coefficient in the open space. One problem to measure D_e by the conductivity method is that the hydrophobic pores in the sample might not be completely wetted, hence the measured resistance would be much greater than the true value.

In this communication we report a novel method to measure the effective diffusion coefficient under atmospheric circumstance, which does not require specially constructed diffusion cell and tracer/carrier gas, nor the analysis of gaseous streams. Both the establishment of oxygen concentration gradient and the determination of the ratio of oxygen concentration difference between the samples are realized in one air-breathing proton exchange membrane fuel cell (PEMFC). The method is validated by comparing the measured N_M value of perforated plates of different diameters with their corresponding theoretical values, and the N_M values of five different GDM were compared with the data acquired from the conventional conductivity method.

2. Methods and material

2.1. N_M measurement – steady-state diffusion method

The steady-state diffusion method was employed to measure the MacMullin number (N_M^t) by comparing the difference of oxygen concentration across the tested samples with that of standard sample under the same oxygen flux, as shown in Fig. 1a. The difference in oxygen concentration across the sample is established and measured in one air-breathing PEMFC with a sample holder in the cathode plate, as shown in Fig. 2a. Multiple holes with diameter of 3.00 mm were drilled in the cathode plate to serve as the passages for oxygen.

The standard sample is a perforated Acrylonitrile Butadiene Styrene (ABS) plate of 2.60 mm in thickness. The sizes and positions of the holes for the standard sample are completely the same as those for the cathode plate. Hence the MacMullin number of the standard sample is 1. The properties of the tested samples (carbon paper) are listed in Table 1. Eight sheets of carbon paper are layered to a total thickness of about 1.6 mm to reduce the measurement error.

The measurements were carried out as follows: (1) record the voltage (E_0) of the PEMFC discharging at a certain current density for 3 min using an Arbin E-load (to avoid water flooding, the cell is operated at a low current density in the range of 150–200 mA cm⁻²); (2) insert the standard sample ($N_M^s = 1$) and record the voltage (E_s) of the PEMFC under the same current density as step 1; (3) keep the standard sample fitted in and insert the tested sample, and then record the voltage (E_t) of the PEMFC under the same current density as step 1. We denote $\Delta E_s = E_s - E_0$ and $\Delta E_t = E_t - E_s$.

The concentration difference ΔC across the samples is equal to the difference in value between the oxygen concentration (C_1) in the catalyst layer without sample in path and that (C_2) with sample (assuming a simple one-dimensional diffusion model). We can deduce the relationship between the voltage difference of the cell and concentration difference from Nernst equation:

$$\Delta E = \frac{RT}{nF} \ln \frac{C_1}{C_2} = \frac{RT}{nF} \ln \left(1 + \frac{\Delta C}{C_2} \right) \quad (2)$$

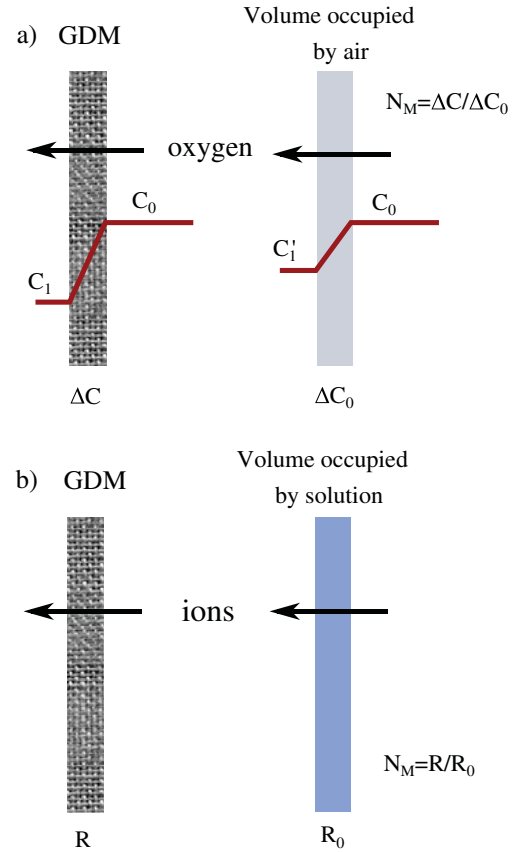


Fig. 1. Illustration of MacMullin number measurement. a) For a steady-diffusion method, N_M is the ratio of the concentration difference with the porous media in the path to that without the porous media. b) For an electrical conductivity method, N_M is defined as the ratio of the resistivity of the porous media filled with electrolyte to the bulk resistance of the same electrolyte.

where R , T , F denote the ideal gas constant, absolute temperature and Faraday's constant. Using the Taylor expansion, we get

$$\Delta E = \frac{RT}{nF} \ln \left(1 + \frac{\Delta C}{C_2} \right) = \frac{RT}{nF} \left(\frac{\Delta C}{C_2} - \frac{1}{2} \left(\frac{\Delta C}{C_2} \right)^2 + \frac{1}{3} \left(\frac{\Delta C}{C_2} \right)^3 + \dots \right) \quad (3)$$

For $\Delta C/C_2$ with a small value, the terms after $\Delta C/C_2$ can be neglected. Hence the concentration difference is proportional to the voltage difference:

$$\Delta C \propto \Delta E \quad (4)$$

Using Fick's law, we find

$$\frac{h_s N_M^s}{h_t N_M^t} = \frac{\Delta C_s}{\Delta C_t} = \frac{\Delta E_s}{\Delta E_t} \quad (5)$$

here h_s , h_t denote the thickness of the standard sample and the test sample, respectively.

2.2. N_M measurement – electrical conductivity method

The method described here is similar to that reported by Martínez et al., in which ion diffusion was used to obtain the effective transport coefficient (see Fig. 1b), and more details can be found in Ref. [16]. The resistivity cell apparatus, as shown in Fig. 2b, consists of a polycarbonate reservoir (15 cm × 10 cm × 10 cm) with a center

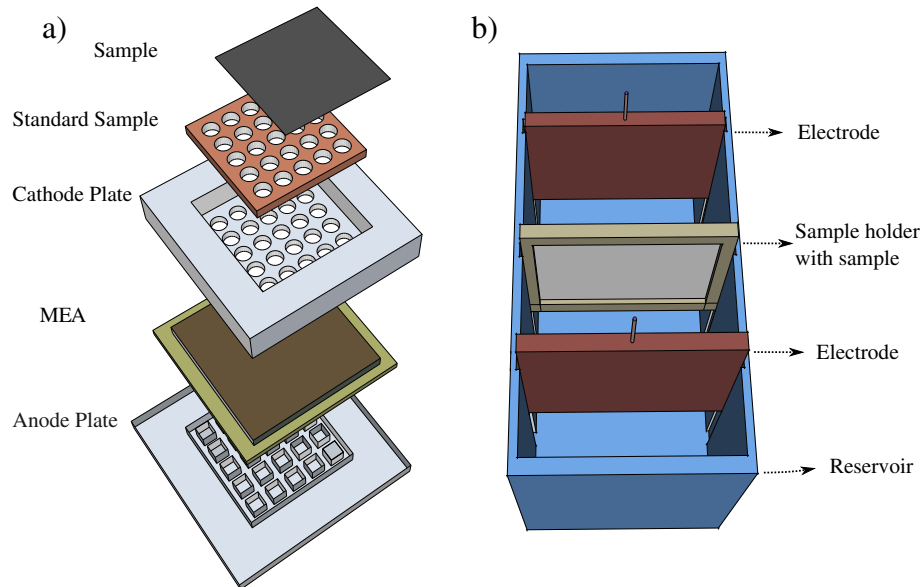


Fig. 2. Scheme of the diffusion cell (a) and resistivity cell (b) used to measure the MacMullin number.

mount sample holder. The cell reservoir was filled with an electrolyte solution consisting of 0.02 M NaCl and 2 M 2-propanol. The samples were placed in the sample holder, and immersed in the reservoir. Two 4 cm × 4 cm graphite plates were placed on the opposite side of the sample with a distance of 1 cm to serve as the working and counter electrodes, respectively.

Before testing, in order to ensure the pores in the sample being wetted, 2-propanol was spread over the sample and the gas bubbles appear on the surface of porous media after immersed in the electrolyte were dabbed with a glassy rod carefully [16]. Then a square-wave form of current was used to measure the resistance with and without the sample in the path. PAR 2273 was used to program the square-wave current oscillating around zero with amplitudes of 10, 20 or 30 mA applied in intervals of 200 ms. The voltage was measured for 200 cycles, and only the last 50 cycles were used to obtain an average voltage to calculate the resistance.

The resistance of electrolyte occupying the same volume as the sample can be written as

$$R_0 = \frac{L}{\sigma_0 A} \quad (6)$$

here L is the thickness of the sample, A is the area of the sample and σ_0 is the conductivity of the electrolyte which can be determined by a conductivity meter. If R_1 represents the resistance of electrolyte with the sample in path, R_2 represents the resistance of electrolyte without the sample in path, then [15]

$$N_M = \frac{R}{R_0} = \frac{R_1 - R_2}{R_0} + 1 \quad (7)$$

3. Results and discussion

Two ABS plates with multiple straight holes sharing the same centers with the holes in the cathode plate, whose diameter are 2.71 mm and 2.47 mm, respectively, were used to validate the measurements of the new method. The MacMullin number was obtained by comparing the concentration difference of oxygen across the plates with standard sample. The theoretical values of MacMullin number are 1.23 and 1.48 (for straight holes, $N_m = \tau/\varepsilon$) [16], while the measured values are 1.17 ± 0.04 and 1.47 ± 0.04 , respectively. It is confirmed that this method is feasible for diffusion coefficient measurement.

Five different GDMs were tested for comparing the results obtained by the proposed method and the conductivity method, and the results are listed in Table 1. The MacMullin numbers of the untreated Toray 060 (A) measured by the resistivity cell and the diffusion cell are 2.22 and 1.82, respectively, while the experimental values of Toray series carbon paper determined by various studies are in the range of 2.80–3.65 [5,9,16–18]. The lower value measured by the novel method might be explained that the diffusion cross section area of the carbon paper is larger than that of the projection of holes in the cathode plate resulting in a low superficial resistance.

For carbon papers with wet-proof treatment (B and C), the MacMullin numbers measured by the resistivity cell are much larger than those measured by the diffusion cell, which might be explained by that the non-wetting hydrophobic pores in the tested sample result in an increase in diffusion resistance for the conductivity method. Oxygen molecules are supposed to be able to diffuse to all the pores in the porous media while ions could only diffuse to the wetting pores, hence the MacMullin number measured by the new method might be more reliable than the conductivity method. Although the PTFE loading for sample B (single side wet-proof) and C (double side wet-proof) is identical, the MacMullin number of sample C is larger than that of B, indicating that double side wet-proof sample has a low permeability. The deviation of MacMullin number between B and C measured by the resistivity cell is larger

Table 1
Summary of the measured MacMullin number for the tested samples.

Label	Description	$N_M^{\text{ion}^a}$	$N_M^{\text{oxy}^b}$
A	Toray TGP-H-060	2.22 ± 0.08	1.82 ± 0.15
B	Toray TGP-H-060 with single side wet-proof (10 wt% PTFE loading)	2.98 ± 0.05	1.98 ± 0.16
C	Toray TGP-H-060 with double side wet-proof (10 wt% PTFE loading)	3.98 ± 0.03	2.19 ± 0.13
D	Sample B with MPL (XC-72:PTFE = 6:4, $0.6\text{mg}_{\text{XC-72}}\text{cm}^{-2}$)	1.24 ± 0.04	3.25 ± 0.28
E	Sample C with MPL (XC-72:Nafion = 9:1, $0.8\text{mg}_{\text{XC-72}}\text{cm}^{-2}$)	0.55 ± 0.03	2.48 ± 0.22

^a Measured by resistivity cell.

^b Measured by diffusion cell.

than that measured by the diffusion cell, suggesting sample C has more non-wetting pores. It shows that samples prepared with PTFE binder have larger MacMullin number than that with Nafion from Table 1, which might be due to the agglomeration behavior of PTFE resulting in a low permeability [19].

It can be seen from Table 1 that the MacMullin number of samples with MPL (D and E) measured by resistivity cell is lower than that without MPL (B and C), which is opposite to the result tested by the novel method proposed in this work. The results reported in literature measured by different methods are conflict. Some researchers show that the addition of MPL decreases the through-plane gas permeability significantly [20], indicating an increase in N_M in samples with MPL, which is consistent with the results measured by the novel method. In contrast, Martínez-Rodríguez et al. found that the MacMullin number measured by the electrical method decreased after adding MPL [21]. They argued that the different wet proofing treatments of the substrate and MPL can cause an additional driving force in the liquid through the pores. However, it is more likely that the abundant pores in the MPL is capable of adsorbing quantities of ions, thus the high local ion concentration lowers the resistance. It is worthy to note that the MacMullin number of sample E is less than 1, which might be due to Nafion ionomer used in MPL enhancing the absorption process.

4. Conclusions

In summary, we develop a simple and effective method to measure the effective diffusion coefficient. In contrast to conventional resistivity method, which requires careful sample preparation and faces the problems of non-wetting pores, the proposed method by which the difference of oxygen concentrations in air could be established and determined in one PEMFC simplifies the procedure of the measurement and enhances the reliability provided that a non-wetting sample was tested.

Acknowledgments

This work was supported by the National Basic Research Programme (No. 2012CB215500) and National High-tech R&D Programme (No. 2012AA053401) of China.

References

- [1] R.B. Bird, W.E. Stewart, E.N. Lightfoot, *Transport Phenomena*, second ed., John Wiley & Sons, Inc., 2002.
- [2] T. Tokunaga, L. Waldron, J. Nemson, *Soil Sci. Soc. Am. J.* 52 (1) (1988) 17–23.
- [3] T. Marrero, E. Mason, *J. Phys. Chem. Ref. Data* 1 (1972) 3–118.
- [4] W. Stewart, S. Gotoh, J. Sorensen, *Ind. Eng. Chem. Fundam.* 12 (1) (1973) 114–118.
- [5] N. Zamel, N. Astrath, X. Li, J. Shen, J. Zhou, F. Astrath, H. Wang, Z. Liu, *Chem. Eng. Sci.* 65 (2) (2010) 931–937.
- [6] J. Shen, J. Zhou, N.G. Astrath, T. Navessin, Z.-S.S. Liu, C. Lei, J.H. Rohling, D. Bessarabov, S. Knights, S. Ye, *J. Power Sources* 196 (2) (2011) 674–678.
- [7] M.V. Williams, E. Begg, L. Bonville, H.R. Kunz, J.M. Fenton, *J. Electrochem. Soc.* 151 (8) (2004) A1173–A1180.
- [8] J. Stumper, H. Haas, A. Granados, *J. Electrochem. Soc.* 152 (4) (2005) A837–A844.
- [9] D.R. Baker, C. Wieser, K.C. Neyerlin, M.W. Murphy, *ECS Trans.* 3 (1) (2006) 989–999.
- [10] J. St-Pierre, B. Wetton, G.-S. Kim, K. Promislow, *J. Electrochem. Soc.* 154 (2) (2007) B186–B193.
- [11] D.R. Baker, D.A. Caulk, K.C. Neyerlin, M.W. Murphy, *J. Electrochem. Soc.* 156 (9) (2009) B991–B1003.
- [12] W.H. Hedley, F.J. Lavacot, S.L. Wang, W.P. Armstrong, *AIChE J.* 12 (2) (1966) 321–327.
- [13] E. Cussler, *Diffusion: Mass Transfer in Fluid Systems*, third ed., Cambridge University Press, 2009.
- [14] M. Wyllie, M. Spangler, *AAPG Bull.* 36 (1952) 359–403.
- [15] R.B. MacMullin, G.A. Muccini, *AIChE J.* 2 (3) (1956) 393–403.
- [16] M. Martínez, S. Shimpalee, J. Van Zee, *J. Electrochem. Soc.* 156 (2009) B80–B85.
- [17] D. Kramer, S.A. Freunberger, R. Fickiger, I.A. Schneider, A. Wokaun, F.N. Bchi, G.G. Scherer, *J. Electroanal. Chem.* 612 (1) (2008) 63–77.
- [18] J.M. LaManna, S.G. Kandlikar, *Int. J. Hydrogen Energy* 36 (8) (2011) 5021–5029.
- [19] Q. Mao, G. Sun, S. Wang, H. Sun, Y. Tian, J. Tian, Q. Xin, *J. Power Sources* 175 (2) (2008) 826–832.
- [20] X. Wang, H. Zhang, J. Zhang, H. Xu, Z. Tian, J. Chen, H. Zhong, Y. Liang, B. Yi, *Electrochim. Acta* 51 (23) (2006) 4909–4915.
- [21] M.J. Martínez-Rodríguez, T. Cui, S. Shimpalee, S. Seraphin, B. Duong, J.V. Zee, *J. Power Sources* 207 (0) (2012) 91–100.